

CLAIMS

1. Polymerizable composition for making thio containing resins comprising,

5 A) at least one polyisocyanate or polyisothiocyanate monomer and at least one polythiol or at least one episulfide compound and optionally one or more compounds having two or more functional groups capable of reacting with episulfide groups; and

B) a polymerization catalyst, wherein the polymerization catalyst comprises an effective amount of at least one salt of formula:



M^p_+ is a cation selected from the group consisting of alkaline metals, alkaline earth metals, transitions metals and ammonium groups of formula NR^+_4 in which R is an alkyl radical,

15 Y^- is an anion such as the corresponding acid YH has a pKa fulfilling the condition $0.5 \leq pKa \leq 14$ with the proviso that when the polymerizable compositions comprise an episulfide compound and M^p_+ is an ammonium group, the polymerizable composition also comprises an electro-donor compound,

20 p is the valency of the cation, and
 $n = mxp$.

2. Polymerizable composition according to claim 1, wherein the associated acid YH has a pKa fulfilling the condition $0.5 \leq pKa \leq 8$.

25 3. Polymerizable composition according to claim 1, wherein Y^- is selected from the group consisting of thiocyanate, carboxylate, thiocarboxylate, RS^- wherein R is a substituted or non-substituted alkyl group or phenyl group, acetylacetonate, diketone, acetoacetic ester, malonic ester, cyanoacetic ester, and ketonitrile.

30 4. Polymerizable composition according to claim 1, wherein the cation M^p_+ is selected from the group consisting of Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Al^{3+} .

5. Polymerizable composition according to claim 5, wherein the ammonium groups NR_4^+ , the alkyl radicals R are selected from the group consisting of $\text{C}_1\text{-C}_8$ alkyls.

5 6. Polymerizable composition according to claim 1, wherein the alkyl radicals R are selected among methyl, ethyl, propyl, butyl and hexyl radicals.

7. Polymerizable composition according to claim 1, wherein the catalyst is present in an amount of 5 to 1000 parts per million (ppm), based on the total weight of the polymerizable monomers
10 present in the composition.

8. Polymerizable composition according to claim 1, further comprising an electrodonor compound enhancing the reactivity of the polymerization reaction.

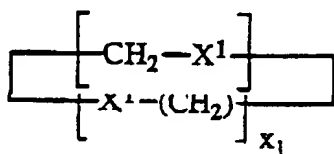
9. Composition according to claim 8, wherein the
15 electrodonor compound is selected from the group consisting of acetonitrile compounds, amide compounds, sulfones and sulfoxides, trialkylphosphites, nitro compounds, ethyleneglycol ethers, crown ethers and kryptates.

10. Composition according to claim 9, wherein the crown
20 ether and the kryptate are selected from the compounds of formulae:

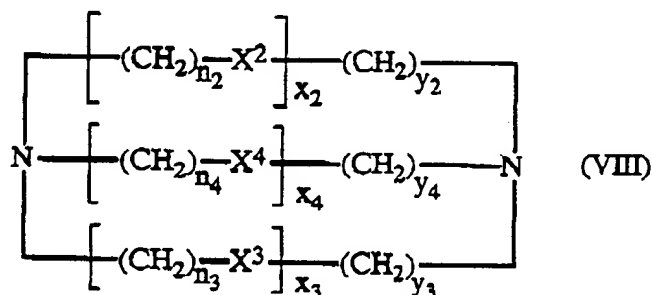
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and



wherein X^1 represents O, S or NH, x_1 is an integer from 3 to 6,

X^2 , X^3 and X^4 represent O or S, n_2 , n_3 , n_4 , y_2 , y_3 , y_4 are 2 or 3, and x_2 , x_3 , x_4 , are 2 or 3.

11. Composition according to claim 9, wherein the electro-donor compound represents up to 5% by weight of the total weight of the polymerizable monomers present in the composition.

12. Composition according to claim 1, further comprising a solvent.

13. Composition according to claim 12, wherein the solvent is a polar organic solvent.

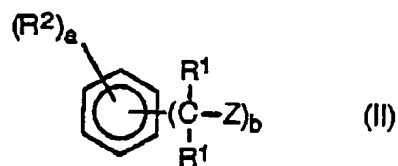
14. Composition according to claim 12, wherein the solvent is a reactive solvent containing one hydroxyl function, one double bond and one hydrogen labile function.

15. Composition according to claim 12, wherein the solvent represents up to 2% by weight, based on the total weight of the polymerizable monomers.

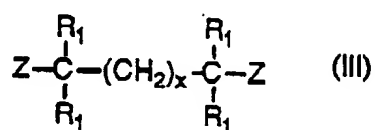
16. Composition according to claim 1, wherein the

polyisocyanate and the polyisothiocyanate monomers are selected from the compounds having the formulae:

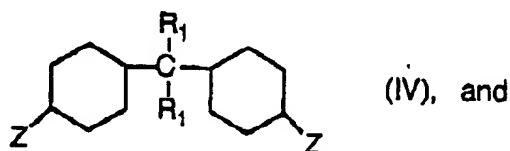
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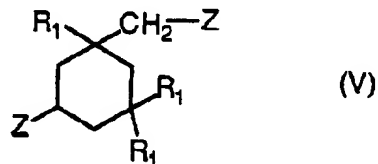
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wherein

R^1 is independently H or a C_1 - C_5 alkyl group;

R^2 is H, an halogen, or a C_1 - C_5 alkyl group;

Z is $-N=C=O$ or $-N=C=S$;

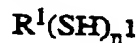
5 a is an integer ranging from 1 to 4, b is an integer ranging from 2 to 4 and $a + b \leq 6$; and

x is an integer from 1 to 10.

10 17. Composition according to claim 13, wherein the polyiso(thio)cyanate monomers are selected from the group consisting of tolylene diiso(thio)cyanate, phenylene diiso(thio)cyanate, ethylphenylene diiso(thio)cyanate, isopropyl phenylene diiso(thio)cyanate, dimethylphenylene diiso(thio)cyanate, diethylphenylene diiso(thio)cyanate, diisopropylphenylene diiso(thio)cyanate, trimethylbenzyl triiso(thio)cyanate, xylylene diiso(thio)cyanate, benzyl triiso(thio)cyanate, 4,4'-diphenyl methane diiso(thio)cyanate, naphthalene diiso(thio)cyanate, isophorone diiso(thio)cyanate, bis(iso(thio)cyanate methyl) cyclohexane, hexamethylene diiso(thio)cyanate and dicyclohexylmethane diiso(thio)cyanate and mixtures thereof.

20 18. Composition according to claim 1, wherein the polyiso(thio)cyanate monomer or the mixture thereof represents 30 to 70% by weight of the total weight of the polymerizable monomers present in the composition.

25 19. Composition according to claim 1, wherein the polythiol has formula:



in which n^1 is an integer from 2 to 6 and R^1 is an organic group of valency equal to n^1 .

30 20. Composition according to claim 1, wherein the polythiol represents 30 to 70% by weight of the total weight of the polymerizable monomers present in the composition.

21. Composition according to claim 1, wherein the salt catalyst or mixture thereof is the sole polymerization catalyst present in the composition.

35 22. Composition according to claim 1, wherein the

composition is a two-component polymerizable composition.

23. Composition according to claim 22, wherein the two component polymerizable composition comprises a first premix containing:

- 5 - the totality of the polyiso(thio)cyanate monomer and optionally
 - part or the totality of the polythiol monomer;
 - a UV absorber; and
 - a mold release agent; and
- 10 a second premix containing:
 - the salt catalyst as defined in claim 1; and eventually
 - part or the totality of the polythiol monomer;
 - a solvent and/or
 - an electrodonor compound.

15 24. Composition according to claim 23, wherein first premix contains, in part by weight:

- 40-100 of a polyiso(thio)cyanate monomer,
- 0-60 of a polythiol monomer;
- 0-0.3 of a UV absorber; and
- 20 - 0-0.2 of an internal mold release agent; and second premix contains, in part by weight:
 - 0-100 of a polythiol monomer;
 - 0-1 of a solvent;
 - 0.001 to 0.01 of a salt catalyst as defined in claim 1; and
 - 25 - 0-5 of an electro-donor compound.

25. Cast article made of a polyurethane resin made of a composition according to anyone of claims 1 to 24 fully polymerized.

26. Process for making a cast polyurethane resin article, characterized in that it comprises:

- 30 - preparing a first premix and a second premix as set forth in claim 23;
 - mixing the first premix and the second premix at room temperature in appropriate quantities;
 - filling a mold with the mixed quantities of first and second
- 35 premix and maintaining at room temperature until a hard gel is

formed; thereafter

- curing the filled mold in an oven at an elevated temperature until complete polymerization; and

- removing the cast article from the mold.

5 27. Process according to claim 26, wherein the weight ratio of first premix over second premix ranges from 4 to 10.

28. Process according to claim 26 wherein mixing time of the first and second premix ranges from 10 to 180 seconds.

10 29. Process according to claim 26, wherein curing is effected at a temperature ranging from 50 to 150°C for 2 to 4 hours.

30. Process according to claim 26, wherein cast article is an optical article.

15 31. Polymerizable composition comprising at least one episulfide compound and, as polymerization catalyst, an effective amount of at least one salt of formula:



wherein

20 M^p_+ is a cation selected from the group consisting of alkaline metals, alkaline earth metals, transitions metals and ammonium groups of formula NR^+_4 in which R is an alkyl radical,

25 Y^- is an anion such as the corresponding acid YH has a pKa fulfilling the condition $0.5 \leq pKa \leq 14$ with the proviso that when the polymerizable compositions comprise an episulfide compound and M^p_+ is an ammonium group, the polymerizable composition also comprises an electro-donor compound,

p is the valency of the cation, and

$n = mxp$.

30 32. Polymerizable composition according to claim 31, wherein the at least one episulfide compound represents 100% by weight of the polymerizable monomers present in the composition.

33. Polymerizable composition according to claim 31, further comprising a polythiol.

35 34. Polymerizable composition according to claim 31, further comprising a crown ether.